July 1996

Model calculations of Langmuir monolayers: Pressure effects on tilting behavior of idealized amphiphiles

D.R. Swanson
University of Nebraska - Lincoln

Robert J. Hardy
University of Nebraska - Lincoln, rhardy1@unl.edu

Craig J. Eckhardt
University of Nebraska - Lincoln, ceckhardt1@unl.edu

Model calculations of Langmuir monolayers: Pressure effects on tilting behavior of idealized amphiphiles

D. R. Swanson
Department of Chemistry, University of Nebraska at Lincoln, Lincoln, Nebraska 68588-0304

R. J. Hardy
Department of Physics, University of Nebraska at Lincoln, Lincoln, Nebraska 68588-0304

C. J. Eckhardt
Departments of Chemistry and Physics, University of Nebraska at Lincoln, Lincoln, Nebraska 68588-0304

Model amphiphiles consisting of lines of Lennard-Jones (LJ) centers are investigated to determine the effect of pressure and molecular geometry on ground-state tilting behavior. Both the amphiphile length and the intramolecular distance between LJ centers is varied. The results give guidelines for understanding and controlling tilting behavior in monolayer films. © *1996 American Institute of Physics.* [S0021-9606(96)51026-3]

INTRODUCTION

Langmuir monolayers have received considerable attention recently in both applied and basic research, with the latter centered around the characterization of the π–T phase diagram of fatty acids and their derivatives.[1–3] Simulations of ever-increasing complexity have been performed with considerable success to aid in understanding the various phases observed.[4] However, the very complexity that leads to numerical accuracy frequently hinders conceptual clarity. At the other extreme, simple models based on planar figures,[5] rigid rods,[6–8] and linear molecules composed of Lennard-Jones centers,[9] have been studied. While these do not reproduce experimental data quantitatively, they do give a clear qualitative picture of the mechanisms governing the complicated behavior of these systems.

Previously we presented a simple cross-section potential that qualitatively models the temperature dependence of the in-plane orientational order of the high-pressure fatty acid phases.[10] The bound-to-free rotator transition found is consistent with the interpretation that the average cross-sectional geometry of the amphiphile dictates in plane packing. Other planar simulations have been applied to study the correlation of intramolecular conformation and crystallization.[5] However, these approaches provide little direct information concerning out-of-plane orientational order. This requires explicit inclusion of the third dimension.

The simplest models involving three-dimensional objects are systems of rigid rods. For example, spherocylinders grafted to a hard two-dimensional lattice have recently been studied.[6] A first-order phase transition from an untilted phase to a next nearest neighbor (NNN) tilted phase was found as the lattice spacing was increased. The expanded lattice had a lower energy than that giving the untilted phase. The lattice expanded in the direction of the tilt and contracted in the perpendicular direction. When a surface potential intended to model amphiphile–subphase interactions was included, a second-order tilt transition occurred with tilt towards nearest neighbors (NN). A weakly first-order transition between NN and NNN tilt directions was also found.

Chemical composition plays no role in the tilting of rigid rods. Instead, tilting is determined by the lattice spacing and the finite length of the cylinders, with the tilt magnitude being inversely proportional to the length.[6] More chemically relevant ''coarse-grained'' models that consist of a linear molecule composed of Lennard-Jones centers, or united atoms, have also been studied.[9] To aid the visualization of these systems, they will be referred to as *beaded strings* (Fig. 1). These systems are simpler than nonlinear united atom models[1] but still allow the dependence of tilting behavior on amphiphile geometry to be investigated.

One previous study[9(b)] fixed the distance between beads, d_0, equal to 1/3 the potential minimum separation r_{pm} (Fig. 1). Various stable packing states consisting of vertical strings, uniformly NNN tilted strings, and nonuniformly tilted strings were found, respectively, as the lattice was expanded. The lattice spacing giving the vertical phase had the lowest energy. The lattice was constrained to remain triangular, although this constraint was released for some calculations in which the lattice distorted to rectangular. Later, off-lattice simulations were performed for beaded strings that were allowed to change conformation.[9(c)] These strings were composed of seven beads with $d_0 = 0.7 r_{pm}$. The ground state (or energy minimum) analysis assumed a uniform tilt on a triangular lattice, and yielded a NNN tilt.

Some remaining problems of a geometrical or chemical nature are investigated here. These include the influence of the length of the string and the value of d_0 on the magnitude and direction of the tilt. Intermolecular interactions, limited to nearest neighbors in the previous work, are calculated to all neighbors within a well-defined cutoff distance. Pressure, which was not directly accounted for,[9] is included here. Uniformly tilted molecules are considered, since they are primarily what is found experimentally[1,11,12] and what simulations give at low temperatures.[9(b),9(c)] Temperature effects, studied previously for some of these systems,[9] are neglected here,
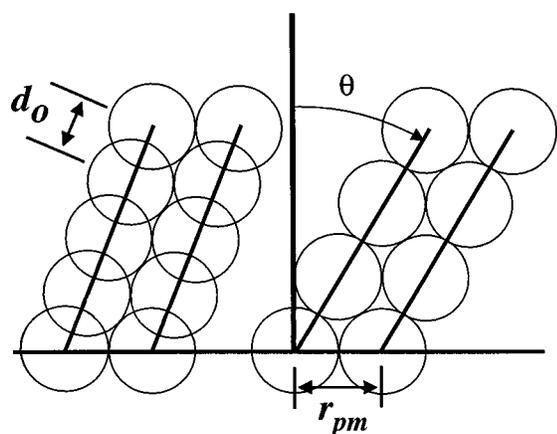
FIG. 1. Illustration of expected effect of d_0 on tilt magnitude.

since we are primarily interested in the effect on the ground state of the intrastring geometry.

Figure 1 shows that the primary geometric parameter characterizing a given beaded string is d_0. To apply this model to fatty acids, the beads must be considered as an averaged, or coarse-grained, group of atoms arising from either orientational or conformational disorder.[9] Cases when d_0 has values of 1 or greater have possible application to amphiphiles such as staffanes,[13] where molecular ''beads'' are linked by single bond ''spacers.''

In all of the cases mentioned above, the same intuitive tilting mechanism is operative. Figure 1 shows that the close-packing principle predicts a tilt for all the studied geometries, i.e., d_0 equal to 0.3, 0.7, 1.0, and 1.4. The first two values allow for comparison to previous results,[9] while the latter two are essentially limiting geometries. Since $d_0=1.0$ corresponds to the van der Waals separation between beads, the system is expected to tilt towards NNN in order to arrive at a three-dimensional hexagonal closest packed (HCP) structure. Note that 1.4 is slightly less than $\sqrt{2}$, the diagonal distance across a square with sides of unit length. A NN tilt would result in an unphysical geometry for values of d_0 greater than $\sqrt{2}$, since some chemical group would connect the beads and sterically prevent such a configuration.

This paper contains three further sections. First the calculational method and potential function are described. Then detailed ground state results are analyzed for dependence upon pressure, amphiphile length, and amphiphile geometry (value of d_0). Finally, the implications these results hold for the synthesis of amphiphile molecules are discussed and suggestions for understanding and controlling amphiphile tilt behavior are made.

CALCULATIONS

Linear strings (or molecules) on a perfect lattice were considered. Each string had the same finite number of beads. No constraint was imposed on lattice symmetry except the restriction to one molecule per unit cell. This limitation is consistent with the assumption of uniform tilt for molecules with radial symmetry, and is consistent with previous low

temperature calculations.[9] Minimum energy configurations were investigated with emphasis on specific important tilt directions, primarily NN and NNN. There is an energy barrier between these two directions, and the two associated local minima were compared to find the thermodynamically favored tilt direction. The effect of isotropic pressure was also investigated.

The energy of the system was minimized with respect to the lattice parameters a, b and γ, and the orientational angles Θ and Φ, where Θ is the tilt angle with respect to the film normal and Φ is the associated azimuthal angle. The lattice parameters were allowed to adjust as the azimuthal angle changed. When the lattice distorts greatly from the original hexagonal lattice, the meaning of the NN and NNN directions is no longer straightforward, so that care must be taken to ensure that these labels are appropriate for a particular minimum. To do this, a gradient minimization was used to find the local minimum nearest to $\Theta=0$ in each of three directions: NN ($\Phi=0$), NNN ($\Phi=90°$), and an intermediate direction ($\Phi=15°$). Using this method, the minimized lattice never distorted far from hexagonal symmetry. Although there are six equivalent directions for any given azimuthal angle for the original hexagonal lattice, the directions listed were the ones actually considered. With them NN tilt is equivalent to a tilt along the x axis and NNN tilt is equivalent to a tilt along the y axis.[14] A local minimum was not always found near one of these directions.

A truncated Lennard-Jones potential was used for the interaction between beads on different strings. The untruncated potential may be written in terms of the distance to the potential minimum r_{pm} as

$$\phi(r) = \epsilon \left(\frac{r_{pm}^{12}}{r^{12}} - \frac{2 r_{pm}^6}{r^6} \right), \qquad (4.1)$$

where r is the distance between the centers of the beads. r_{pm} is related to the hard core diameter σ by $r_{pm}=2^{1/4}\sigma$. Both ϵ and r_{pm} were set equal to 1. The potential was smoothly truncated beginning at a reduced distance of 2.0. The exact form used was

$$\Phi_c(r) = \begin{cases} -a(r^2 - r_d^2)^2 & r_c < r \leq r_d \\ 0 & r > r_d \end{cases}, \qquad (4.2)$$

where $r_c=2.0$, $r_d=2.586\,084\,045$ and $a=0.004\,291\,804\,757$ r_d and a were chosen to make the potential and its first derivative continuous. Since the energy differences between the different minima and saddle points were often small, the details of the potential can be quite important.

TABLE I. Length dependence of preferred tilt direction at zero pressure.

d_0	NN	NNN	Vertical	Intermediate
1/3		>20 beads	<20 beads	>20 beads (hex lattice)
0.7	>12 beads	<12 beads		
1.0		All lengths		
1.4		All lengths		

TABLE II. Pressure dependence of preferred tilt direction. Length=15 beads.

d_0	NN	NNN	Vertical	Intermediate
1/3		Pressure<100	Pressure≥100	
0.7		Pressure≥100	Pressure≥10^4	10^3≤pressure≤10^4
1.0		All pressures		
1.4		Pressure≤10^3		Pressure≥10^3

RESULTS

The results are summarized in Tables I and II. The preferred tilt direction for $d_0<1$ and zero pressure is found to be length dependent. The global energy minimum configuration is vertical ($d_0=1/3$) or tilted towards NNN ($d_0=0.7$) for short lengths and is tilted towards NN for longer lengths. A NNN tilt for smaller values of d_0 on an unconstrained lattice agrees with results from rigid rod calculations.[6] Also in agreement is the lattice expansion in the direction of the tilt and contraction in the perpendicular direction. The vertical phase agrees with the report[9(b)] of a global vertical minimum for strings with $d_0=1/3$ and 15 beads in length. Significant tilt angles were not found until the string was extended to greater than 20 beads (Fig. 2). This may be understood by considering two Lennard-Jones atoms which have a separation equal to the potential minimum value of r_{pm}. Constraining two diatomics to remain vertical gives a separation between molecules that is smaller than r_{pm}. This type of configuration is impossible in a diatomic hard sphere system with spheres of diameter r_{pm}. It is related to the somewhat counterintuitive result that the vertical phase for short strings with $d_0=1/3$ is the phase that minimizes the energy. As the amphiphiles get longer, the amount of overlap increases, so that the repulsive part of the potential begins to dominate and forces a collective tilt. This is not equivalent to a pressure effect, since to treat pressure a pressure–volume term must
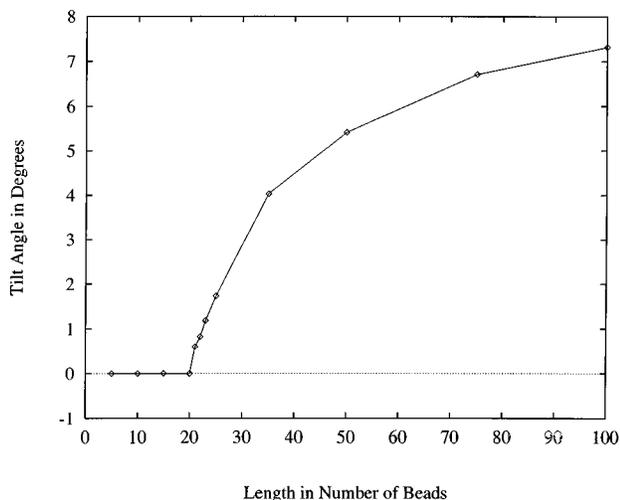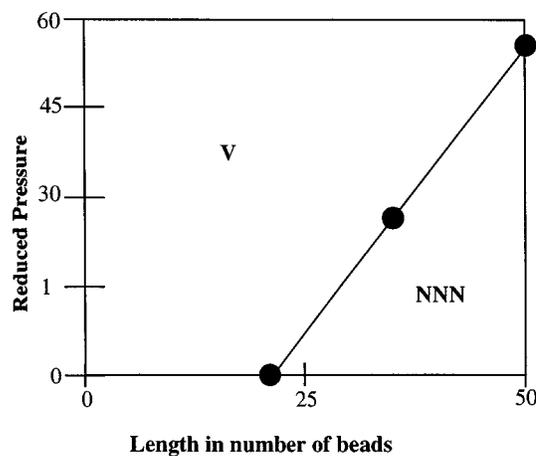
FIG. 3. Length–pressure phase diagram for $d_0=1/3$. Circles are calculated results. V for vertical tilt. NNN for next nearest neighbor tilt.

be included in the energy. Isotropic pressure simply increases the length necessary for NNN tilt to occur (see Fig. 3).

When the $d_0=1/3$ system was constrained to a hexagonal lattice, the minimum energy was consistently found to be a system tilted in an intermediate direction ($\Phi\approx130°-140°$). This was true for all strings calculated that consisted of more than 20 beads. This is attributed to the symmetry of a hexagonal lattice, for which there is no preferred tilt direction until the lattice distorts.[14]

The case of $d_0=0.7$ is more complicated. The minimum energy configuration for lengths shorter than 12 beads is tilted towards NNN, in agreement with previous results,[9(c)] but for longer lengths is tilted towards NN. These two tilt directions define local minima for this system for lengths greater than ten beads. The difference in energy between these two local minima versus string length is shown in Fig. 4. NN energies for lengths of ten beads or less were calculated with Φ fixed at 0. Since the NN minima have a larger area per string than the NNN minima, either one may be selected by applying an appropriate pressure for a given length string. As the pressure is increased, the local minimum for the NN phase disappears altogether. The pressure dependence of this geometry of a beaded string is diagrammed in Fig. 5.

Pressure affects both the direction and the magnitude of the tilt, although the pressure required to produce a vertical phase is orders of magnitude larger than that required to alter the tilt direction. As the vertical phase pressure is approached, the lattice becomes increasingly hexagonal, and behavior analogous to that seen for the $d_0=1/3$ system constrained to a hexagonal lattice is exhibited. The tilt direction for the minimum energy state at these reduced tilt angles is again in an intermediate direction (Fig. 5).

The proximity of the intermediate tilt phase to the vertical phase is suggestive of the pressure dependence seen in the fatty acid phase diagram for the L_1' phase. The $d_0=0.7$ system thus contains the same progression of tilt phases as do the fatty acids: NN at low pressure, NNN at increased

FIG. 2. Tilt behavior for $d_0=1/3$ strings of various lengths at zero pressure.
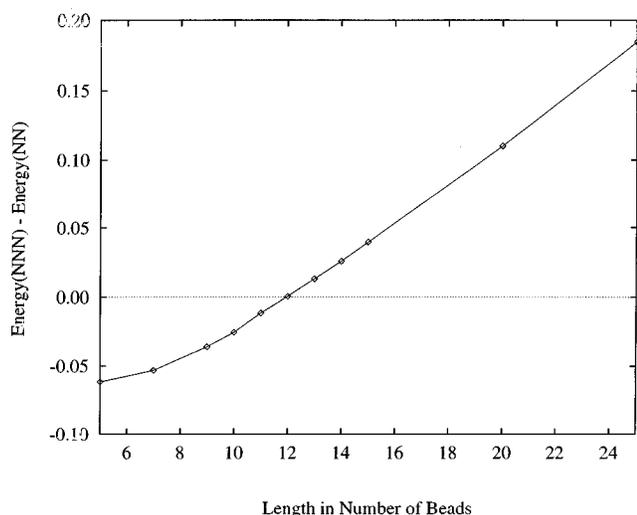
FIG. 4. Preferred tilt direction plot for $d_0=0.7$ strings of various lengths. Negative energy differences indicate NNN tilt, positive energy differences indicate NN tilt. The energy at zero energy difference is -96.773.

pressure, and vertical at high pressure. However, the orders of magnitude difference between the pressure necessary to change the tilt direction and that required to eliminate tilt does not scale well to the observed fatty acid phase diagram. This can be improved by incorporating temperature effects, since it has been shown that tilt magnitude is reduced with
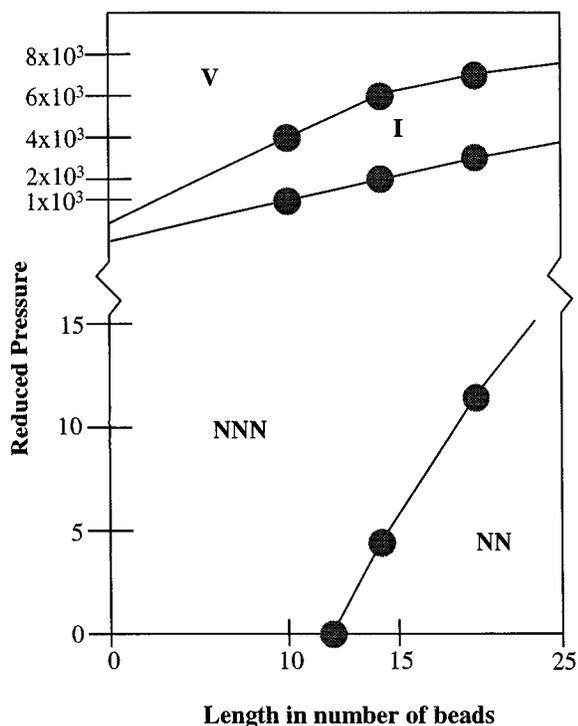

FIG. 5. Length–Pressure phase diagram for $d_0=0.7$. Circles represent calculated results. V for vertical, I for intermediate, NNN for next nearest neighbor, and NN for nearest neighbor tilt.

increasing temperature for both rigid and conformationally labile systems.[6,9(c)]

The minimum energy tilt direction changes at $d_0=1$ from NN to NNN. At this value of d_0 the system is essentially that of layered HCP spheres, which is stable for all tested reduced pressures (up to 10^7). The magnitude of tilt decreased only slightly over this range. When d_0 was increased to 1.4, the tilt direction was again towards NNN for pressures up to 10^3. Intermediate tilt directions became preferred at higher pressures, although again the tilt magnitude decreased only slightly for pressures up to 10^7.

DISCUSSION

These studies suggest possibilities for obtaining greater control of tilting behavior in Langmuir monolayers. By varying d_0 and the length of the molecule through appropriate synthesis, the tilt magnitude and direction can be controlled. A qualitative picture of three types of amphiphiles may be proposed: (1) *Smooth amphiphiles*, such as rigid rods or those with $d_0 \leq 0.3$, are vertical under finite pressure and then pack according to their cross sections. An example of such amphiphiles has been reported.[15] (2) *Discrete amphiphiles*, such as staffanes or those with $d_0 \geq 1.0$, have their packing controlled by their various protrusions. In the above example, the vertical portion of the phase diagram is eliminated by locking in a tilted phase. Amphiphiles with alternating protrusions have been reported to exhibit an interlocked vertical intermolecular packing, resulting in extremely rigid films.[16,17] The staffanes have been reported to pack in a vertical phase, which has been attributed to loss of surface planarity through the displacement of subphase ions.[13] (3) *Corrugated amphiphiles*, such as those with $d_0=0.7$, exhibit an overlapped surface that yields a much richer phase diagram. Significant pressure is required to force these amphiphiles to pack vertically, but it is routinely obtainable. The potential energy surface is shallow enough to allow for a multiplicity of phases. In particular, the potential energy surface of fatty acids is quite delicate, as evidenced by the extreme importance of subphase purity for the observance of several fatty acid phases. It therefore appears fatty acids fall into this regime, as demonstrated by the agreement between their qualitative tilt behavior and that of these model systems.

The preferred tilt direction of systems with $d_0<1$ can be altered by sufficient pressure. There is a rotational barrier between the states with NN tilt and those with NNN tilt that can be overcome by sufficient temperature. If the resultant precessing phase was analogous to the LS phase of fatty acids, the molecules would only be vertical on average, but actually tilting in all possible directions with magnitudes bounded by some maximum tilt angle. Experimental evidence is only compatible with this interpretation for small tilt angles, since film thickness estimates indicate vertical molecules.[18]

The pressure dependence of the model is in qualitative agreement with the fatty acid phase diagram for $d_0=0.7$, but does not scale quantitatively. Contributing to this is certainly the highly idealized model potential, but it may indicate that

temperature-induced nonuniform tilt and conformational lability are required to accurately reproduce experimental results. For this highly idealized model, the bottom of the potential energy surface is very flat. It is therefore essential to allow for the distortion of the lattice.

In summary, model beaded string amphiphiles of several geometries have been investigated to determine their ground-state tilting behavior with respect to an external hydrostatic pressure. Smooth amphiphiles exhibit a vertical phase under finite pressure, while discrete amphiphiles are always tilted. In between, corrugated amphiphiles of even these highly idealized molecules display a rich phase diagram qualitatively similar to the fatty acid π–T phase diagram.

ACKNOWLEDGMENT

[1] C. M. Knobler and R. C. Desai, Annu. Rev. Phys. Chem. **43**, 207 (1992).

[2] A. Ulman, *An Introduction to Ultrathin Organic Films, from Langmuir–Blodgett to Self-Assembly* (Academic, San Diego, 1991).

[3] *Langmuir–Blodgett Films*, edited by G. G. Roberts (Plenum, New York, 1990).

[4] For example, S. Shin, N. Collazo, and S. A. Rice, J. Chem. Phys. **98**, 3469 (1993); S. Karaborni and S. Toxvaerd, *ibid.* **97**, 5876 (1992); J. P. Bareman and M. L. Klein, J. Phys. Chem. **94**, 5202 (1990).

[5] D. P. Fraser, M. J. Zuckermann, and O. G. Mouritsen, Phys. Rev. A **43**, 6642 (1991).

[6] V. M. Kaganer, M. A. Osipov, and I. R. Peterson, J. Chem. Phys. **98**, 3512 (1993).

[7] D. Kramer, A. Ben-Shaul, Z.-Y. Chen, and W. M. Gelbart, J. Chem. Phys. **96**, 2236 (1992).

[8] Z.-G. Wang, J. Phys. (Paris) **51**, 1431 (1990).

[9] (a) M. Kreer, K. Kremer, and K. Binder, J. Chem. Phys. **92**, 6195 (1990); (b) M. Scheringer, R. Hilfer, and K. Binder, *ibid.* **96**, 2269 (1992); (c) F. M. Haas, R. Hilfer, and K. Binder, *ibid.* **102**, 2960 (1995).

[10] D. R. Swanson, R. J. Hardy, and C. J. Eckhardt, J. Chem. Phys. **99**, 8194 (1993).

[11] R. M. Kenn, C. Bohm, A. M. Bibo, I. R. Peterson, H. Mohwald, J. Als-Nielsen, and K. Kjaer, J. Phys. Chem. **95**, 2092 (1991).

[12] B. Lin, M. C. Shih, T. M. Bohanon, G. E. Ice, and P. Dutta, Phys. Rev. Lett. **65**, 191 (1990).

[13] H. C. Yang, T. F. Magnera, C. Lee, A. J. Bard, and J. Michl, Langmuir **8**, 2740 (1992).

[14] T. M. Luty and C. J. Eckhardt, J. Phys. Chem. **99**, 8872 (1995).

[15] C. J. Eckhardt, N. M. Peachey, and D. R. Swanson, J. M. Takacs, M. A. Khan, X. Gong, J.-H. Kim, J. Wang and R. A. Uphaus, Nature (London) **362**, 614 (1993).

[16] C. J. Eckhardt, N. M. Peachey, and D. R. Swanson, Langmuir **8**, 2591 (1992).

[17] C. J. Eckhardt, N. M. Peachey, and J. M. Takacs, Thin Solid Films **242**, 67 (1994).

[18] R. M. Kenn, C. Bohm, A. M. Bibo, I. R. Peterson, H. Mohwald, J. Als-Nielsen, and K. Kjaer, J. Phys. Chem. **95**, 2092 (1991).